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PHYSICOCHEMICAL PROPERTIES OF HYDROXYLAPATITE PRODUCED BY PRECIPITATION

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An integrated physicochemical study of hydroxylapatite produced by the wet method is carried out. The possibility of using the material in bioceramics as well as in catalytic and sorption processes as catalyst and sorbent is demonstrated.

The chemical composition of calcium hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (HA) is similar to the main mineral components of the bone tissue of mammals. The function of the regulator of the content of calcium and phosphorus in an organism and the high biological compatibility of HA allow for its extensive use in production of bioceramics [1 – 3]. The purpose of the present study is to evaluate the effect of the temperature of precipitation of hydroxylapatite on its physicochemical properties.

In the present study, HA was obtained by the wet method, i.e., by treatment of aqueous suspension of calcium carbonate with phosphoric acid solution and subsequent introduction of aqueous alkali solution (patent application RF 99113485). The experiment was performed within the temperature range of 25 – 95°C for 90 min with pH of the reaction medium equal to 12. The synthesis of HA under the specified conditions was accompanied by the study of the precipitate using the methods of chemical and local x-ray spectral and x-ray phase analysis, which made it possible to determine the chemical and phase composition of the end product for each synthesis. In addition to that, the IR spectral, electron microscope, and granulometric analysis of the precipitates was carried out.

The content of calcium ions in the end product was determined by complex ionometric titration, and the content of phosphate ions was found by the spectrophotometric method. The local x-ray spectral analysis was performed using a Ling system installed on a CamScan microscope. The IR spectra of the end products were obtained on a SPECORD-75 IR spectrophotometer in analyzing the samples tableted in KBr; the phase composition of the precipitate was analyzed by the x-ray method using a DRON-3 general purpose diffractometer in CuK_α radiation. To measure the dispersion of the obtained HA powders, the dynamic light diffusion method

was used on a MASTERSIZER diffraction ultrasonic laser analyzer. The electron microscope analysis of powders was carried out on a BS-301 scanning microscope. The specific surface area was determined by the thermal nitrogen desorption method on a GKH-1 unit using a gas chromatograph.

The integrated physicochemical analysis of the precipitates made it possible to identify the effect of the precipitation temperature in the chemical, phase, and granulometric compositions of HA.

An increase in the precipitation temperature from 25 to 65°C leads to an increase in the Ca : P ratio in the samples, whereas a further increase in the temperature up to 95°C insignificantly alters this ratio (Table 1). Within the entire investigated temperature interval, the Ca : P ratio virtually correlated with the Ca : P ratio in HA.

Thus, the precipitation product represents HA without significant impurities of other phases, which is corroborated by the x-ray analysis data (Fig. 1a).

X-ray phase analysis of the precipitates indicates that the precipitated product is HA (card 09-432, 34-0010 in the JCPDS system). An increase in the precipitation temperature results in an increased degree of crystallization of the main phase. The intensities of all obtained precipitates in the re-

TABLE 1

Precipitation temperature, °C	Mass content, %		
	Ca	P	Ca : P
<i>Chemical analysis</i>			
25	35.56	18.09	1.85
65	35.88	18.96	1.89
95	35.97	18.54	1.94
<i>Local x-ray spectral analysis</i>			
25	34.76	18.35	1.89
65	37.23	18.87	1.97
95	36.24	18.99	1.92

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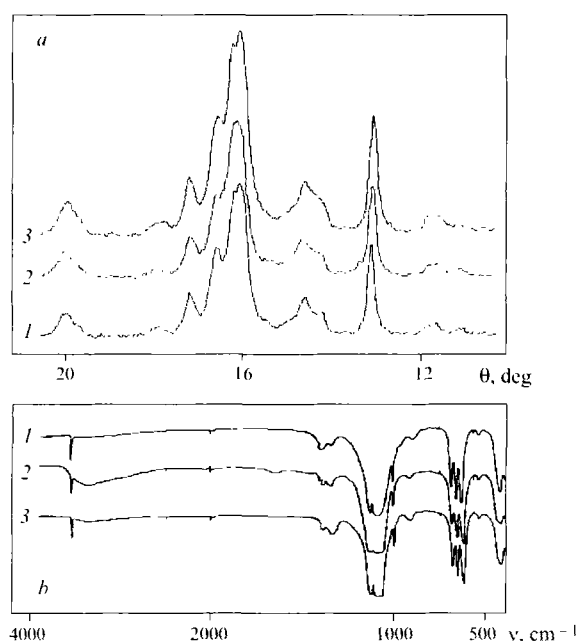


Fig. 1. X-ray patterns (a) and IR spectra (b) of HA at precipitation temperatures 25°C (1), 65°C (2), and 95°C (3).

flexion regions 2.81, 2.77, and 2.72 Å do not correspond to those in the database. Thus, at reflection 2.77 Å, the line intensity is 60% higher, and at reflection 2.72 Å it is 30% lower, than the values specified in the database. In our opinion, this is caused by the presence in the precipitate of a phase which is structurally similar to HA. This phase was identified (card 19-0272 in JCPDS system) as carbonate apatite $\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{OH}$ (2.78, 2.68, 2.62 Å), whose content is 2–3 wt.%.

The x-ray phase analysis results correlate well with the IR-spectroscopy data (Fig. 1b). The low crystallization of the precipitates obtained at temperature 25°C is characterized on the IR spectra by non-split bands in the phosphate ion vibration region. An increase in the temperature from 25 to 95°C leads to a higher degree of crystallization of HA; and perceptible splitting of these bands is observed on the IR spectra. The bands at 3572, 630, and 342 cm^{-1} are caused by the presence of OH^- groups, whereas bands 1087, 1072, 1032, 962, 601, 571, and 471 cm^{-1} are due to various forms of PO_4^{3-} groups. The wide band at 3700–2500 cm^{-1} is determined by the presence of adsorbed H_2O in the precipitates. The presence of the absorption bands at 1420 and 870 cm^{-1} in all powder spectra points to the presence of CO_3^{2-} ions in the precipitate, which agrees well with the x-ray phase analysis data.

The granulometric analysis of HA (Fig. 2) indicates that as the precipitation temperature grows from 25 to 95°C, the predominant particle size increases from 5 to 30 μm . The HA precipitated at 25°C exhibits a uniform size distribution of particles. This agrees with the results of the electron micro-

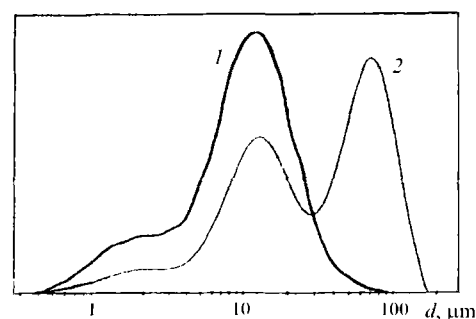


Fig. 2. Size distribution of HA powder particles at precipitation temperatures 25°C (1) and 95°C (2).

scope analysis: HA has the form of rounded grains 3–5 μm in size which consist of smaller round particles of size 300–400 nm. As the precipitation temperature increases to 95°C, the rounded grains become larger and at the same time, agglomerates, and secondary finely dispersed crystals emerge due to the recrystallization processes in the system and the growth of large crystals at the expense of small ones. The secondary crystals consisting of individual particles 300–400 nm in size virtually completely overlap the larger rounded crystals which reach sizes of 30–40 μm . This agrees with the results of the granulometric analysis. Figure 2 shows two extrema which are determined by the polydispersion of the obtained material.

As the precipitation temperature grows from 25 to 65°C, the specific surface area of HA precipitate varies insignificantly and amounts to 85 m^2/g . A further increase of the temperature to 95°C decreases this parameter down to 50 m^2/g . The decrease in the specific surface area of HA is related to the agglomeration processes and increased size of precipitated particles.

The integrated physicochemical analysis of hydroxylapatite produced by the proposed method (RF patent application No. 99113485) shows that its chemical, phase, and granulometric compositions, morphology, and specific surface area facilitate the high reactivity of the material. This makes it possible to use this material in bioceramics, as well as in catalytic and sorption processes as catalyst or sorbent.

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